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(54) ELECTRODEPOSITION OF METALS AND ALLOYS

(71) We, OXY METAL FINISHING (EUROPE) S.A., of 65, Avenue de l'Etang, Châtelaine, 1211 Geneva, Switzerland, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to the electrodeposition of metals and their alloys and is particularly concerned with the electrodeposition of copper, nickel, cadmium and cobalt.

A variety of types of electroplating solutions are at present in use. For example, for the electrodeposition of copper, there are at present employed acidic solutions for high speed plating, pyrophosphate solutions, fluoroborate solutions and cyanide solutions. Each of these solutions has, however, certain disadvantages. For example, acidic solutions tend to corrode the substrate metal to be plated and hence there is the requirement that the substrate should first be coated with another metal which is resistant to the acid in the plating solution.

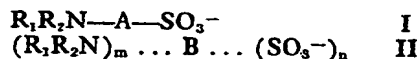
If one is using a neutral or basic electroplating solution, one is not normally faced with corrosion of the substrate. However, the use of pyrophosphate solutions normally results in low deposition rates whereas fluoroborate solutions are not only corrosive but they are also highly toxic. Cyanide solutions tend to give the best operating results not only with regard to operating costs and simplicity of operation but also with respect to the quality of the deposited coating. For example, the lustre, uniformity, homogeneity, adhesion properties and mechanical strengths of the coatings obtained using cyanide plating solutions are very good (see, for example, J. Electrochem. Soc. (1971) page 291 C). However, the use of cyanides is hazardous because of the high toxicity of such compounds and, of course, there are not only the operating problems associated with the use of highly toxic materials, but also the problems associ-

ated with the disposal of an effluent which is also highly toxic.

Many attempts have accordingly been made in the past to produce non-toxic, economical, neutral or basic electroplating solutions which will have the operating advantages of cyanide solutions. A number of such solutions have been proposed, for example, solutions containing a high proportion of ammonia or organic amines such as ethylenediamine (see Gmelin's Handbuch, Kupfer Teil A. page 1194; Handbuch der Galvanotechnik II, 1966, page 84, Karl Hauser Verlag, Munich). Such solutions are, however, less convenient to use than cyanide solutions and they are only usable for the deposition of copper or cadmium coatings but not for nickel or cobalt coatings. Such solutions have also been highly sensitive to any impurity in the plating bath, but they have been more expensive than cyanide solutions, the resistance of the solution has been higher and difficulties have been encountered in obtaining fault-free deposits.

It is accordingly an object of the invention to provide an improved electroplating solution which can be used, in particular, for the plating of cadmium, nickel, cobalt and copper coatings.

According to the invention there is provided an aqueous alkaline cyanide-free electroplating solution which includes a sulphur-free organic amino compound together with a sulphonate of Formula I or Formula II as set out below:—



wherein A is a single bond between N and S or a linear or branched aliphatic radical containing up to 12 carbon atoms, B is a mono- or poly-cyclic aromatic or cycloaliphatic radical containing from 5 to 14 carbon atoms, R₁ and R₂ are radicals, identical or different, selected from hydrogen and alkyl radicals containing from 1 to 6 carbon atoms, n and m

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are each equal to 1, 2 or 3 and each of the interrupted lines represents 1, 2 or 3 valency bonds.

The electroplating solution can include chloride ions which are provided by incorporation of at least one organic amine hydrochloride in the solution. The compound of Formula I can be sulphamic acid, taurine, (i.e. $\text{H}_2\text{N}-\text{CH}_2-\text{CH}_2-\text{SO}_3\text{H}$) or a homologue thereof. The compound of Formula II can be a mono-, di- or tri-aminobenzene-, -naphthalene- or -anthracene mono-, di- or trisulphonic acid. The preferred compounds of Formula II are sulphanilic acid, 1 - aminobenzene - 2 - sulphonic acid and 2 - naphthylamine - 4,8 - disulphonic acid.

The incorporation of compounds of Formula I or Formula II in the electroplating solution improves the physical properties of deposited metals and alloys, particularly with respect to homogeneity, physical strength, ductility and surface appearance. The concentration of the added compounds can be varied considerably. For example, the addition of 0.5 g/l of taurine produces noticeable effects as regards the homogeneity and lustre of the deposited coatings. Higher concentrations can be used and the preferred range for taurine is between 1 and 10 g/l.

The sulphur-free organic amino compound can be one or more of the mono-, di- and poly-amines commonly used as chelating agents in electroplating solutions. Examples of the amines which can be used are ethylenediamine, diethylene triamine, tetramethylethylenediamine, triethylene tetramine, triethanolamine, propylene diamine, cyclohexylamine and diamino cyclohexane. Other usable amines can be found, for instance, in *Modern Coordination Chemistry* by J. LEWIS & R. G. WILKINS, Intersec. Publ. New York (1960), particularly page 13. The amines can be added free or as salts with common organic or inorganic acids, e.g. HCl , H_2SO_4 , H_3PO_4 , AcOH , etc.

The metal or metal components of the alloy to be deposited is or are included in the electroplating solution as a soluble salt of low toxicity, preferably one of the salts commonly used in the electroplating industry; examples of the salts which can be used are sulphates, sulphamates, halides and acetates. If the metal to be deposited is copper, copper sulphate is preferably used because of its cheapness and ready availability. The concentration of metal ions in the plating solution can be varied considerably depending on the end use, the required plating rate and the plating conditions, the concentration being varied, for example, from 1 to 100 g/l.

It has been found that the incorporation of chloride ions in the plating solution increases the operating efficiency of the plating process. Thus the addition of chlorides increases the conductivity of the electroplating

solution with a consequent increase in the current density and thus of the rate of plating. The addition of chlorides, even in very small amounts, for example within the range of from 0.1 to 5 g/l is of advantage. The chloride ions are preferably afforded by the addition to the plating solution of a hydrochloride of an organic base, for example, a lower aliphatic primary, secondary or tertiary mono-, di- or poly-amine. Specific materials which can be used are trimethylamine hydrochloride, diethylamine hydrochloride and butylamine hydrochloride.

The plating solutions of the invention are used for the electrodeposition of metals, particularly of copper, on metallic parts or workpieces and on other conducting materials, for example, insulating substrates which carry a deposited coating of a conducting material. The components to be plated can have any number of different shapes and are arranged as the cathodes in a plating bath. The pH can be between 7.01 and 14, preferably from 7.5 to 10 and the temperature can be between room temperature and 80°C . The temperature at which plating is carried out is not critical but it has been found that if the temperature is low the rate at which plating is carried out can be too low, whereas if the temperature is high, some of the constituents of the plating solution may evaporate. The power supply may be DC or periodically reversed DC. During reversal, the plated parts become anodes and during this anodic phase phenomena are encountered which seem to improve the physical properties of the electrolytic coating. The length of the anodic phase is preferably not more than one sixth the length of the cathodic phase with the amplitude of the anodic phase current either equal to or less than the amplitude of the cathodic phase current.

The invention will now be described by way of example with reference to a number of embodiments thereof. The temperatures which are mentioned are in degrees Centigrade and the concentrations of the various materials are in g/l. The amounts of the metals or alloys to be plated are, when specified, in grammes of free metal.

Example 1.

Electrodeposition of copper.

An aqueous alkaline plating solution for the electrodeposition of copper was prepared by dissolving the following ingredients at the specified concentrations:—

$\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$:	100 g (25.45 g Cu/l)
Ethylenediamine:	80 ml (2.97 mole/l)
Taurine:	5 g (0.099 mol/l)
Triethanolamine:	6 g (0.1 mole/l)
Ethylenediamine:	
HCl :	0.5 g (0.093 mole/l)
Ethylenediamine sulphate:	20 g (0.32 mole/l)

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Ten litres of the above solution were placed in an electrolytic cell. A mobile electrolytic copper anode and a mobile stainless steel cathode, in the form of a rectangular plate, were introduced into the bath. The surface-ratio anode to cathode was 1:4 and the distance between the electrodes was between 5 and 10 cm. The electrodes were moved and the plating solution circulated through a filter by means of a pump which operated continuously during the plating experiments.

The plating solution was heated to 50° and a voltage was applied to the electrodes which was such as to result in a current density of 4 A/dm². Plating was carried out for 20 minutes; after which the cathode was removed and the coating subjected to testing which

gave the following results: hardness: 115—120 kg/mm² (Vickers); purity: 99.99% (by complex formation); thickness: 15 μ; appearance: shiny, uniform, homogeneous; cathode yield: between 90 and 95%.

Example 2.

Electrodeposition of copper.

Two solutions for the electrodeposition of copper were prepared as in Example 1 but the first containing all the ingredients in double concentration (Solution A) and the second containing all the ingredients in triple concentration (Solution B).

Electroplating experiments were conducted as in Example 1 with the following results:

	Vickers Hardness	Purity (%)	Thickness	Yield (%)
A	115—120	99.9	25 μ	85—90
B	115—120	99.9	35 μ	85—90

The appearance of the deposits were the same as observed for the sample of Example 1.

Example 3.

Electrodeposition of Nickel.

A solution for the electrodeposition of nickel ingredients in distilled or deionised water to make a litre of solution. (Nickel is given in weight of pure metal).

NiCl ₂ · ethylenediamine	50
Taurine	10
Triethanolamine	8

The pH of the solution was adjusted to between 8.5 and 9 with H₂SO₄ or ethylenediamine depending on whether the pH had to be reduced or increased.

The electrodeposition of nickel was carried out as described in Example 1 using a nickel anode and operating at 60° C. with a current density between 2 and 4 A/dm². Shiny and homogeneous nickel deposits were obtained the thickness of which could be several tenths of microns.

Example 4.

Electrodeposition of cobalt.

A solution for the electrodeposition of cobalt was prepared as described in Example 3 but replacing the nickel complex by an equivalent amount of CoCl₂ · 2 ethylenediamine. The plating experiments were carried out as in Example 1 with platinised titanium anodes at 50° C. and a current density of 2 A/dm². The coatings were excellent and very shiny.

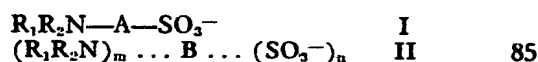
Example 5.

Electrodeposition of cadmium.

A solution for the electrodeposition of cadmium was prepared as in Example 3 but replacing the nickel complex by an equivalent amount of CdSO₄ · 3 ethylenediamine. Plating was carried out as in Example 1, using cadmium anodes at 50° C. and a current density between 1 and 2 A/dm². The coatings obtained had an excellent penetration resistance.

WHAT WE CLAIM IS:—

1. An aqueous alkaline cyanide-free electroplating solution which includes a sulphur-free organic amino compound together with a sulphonate of Formula I or Formula II as set out below:—



wherein A is a single bond between N and S or a linear or branched aliphatic radical containing up to 12 carbon atoms, B is a mono- or poly-cyclic aromatic or cycloaliphatic radical containing from 5 to 14 carbon atoms, R₁ and R₂ are radicals, identical or different, selected from hydrogen and alkyl radicals containing from 1 to 6 carbon atoms, n and m are each equal to 1, 2 or 3 and each of the interrupted lines represents 1, 2 or 3 valency bonds.

2. An electro-plating solution according to claim 1 containing a copper, nickel, cobalt or cadmium salt, said solution being for the

plating of copper, nickel, cobalt or cadmium respectively.

3. An electro-plating solution according to claim 1 or 2 which includes chloride ions.

5 4. An electro-plating solution according to claim 3, wherein said chloride ions are provided by incorporation of at least one organic amine hydrochloride in the solution.

10 5. An electro-plating solution according to any preceding claim, wherein the compound of Formula I is taurine.

6. An electro-plating solution according to claim 5, wherein the amount of taurine in the solution is more than 0.5 g./l.

15 7. An electro-plating solution according to any preceding claim, wherein the sulphur-free amino compound is either ethylene diamine or triethanolamine.

20 8. An electro-plating solution according to any preceding claim which contains between 1 and 100 g./l. of copper as copper sulphate.

9. A method of electro-plating which includes the use of an electro-plating solution according to any one of claims 1 to 7.

10. A method of copper electro-plating 25 which includes the use of a plating solution according to claim 8.

11. An electro-plating solution substantially as hereinbefore described with reference to any one of the Examples. 30

12. A method of electro-plating which includes the use of an electro-plating solution substantially as hereinbefore described with reference to any one of the Examples.

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